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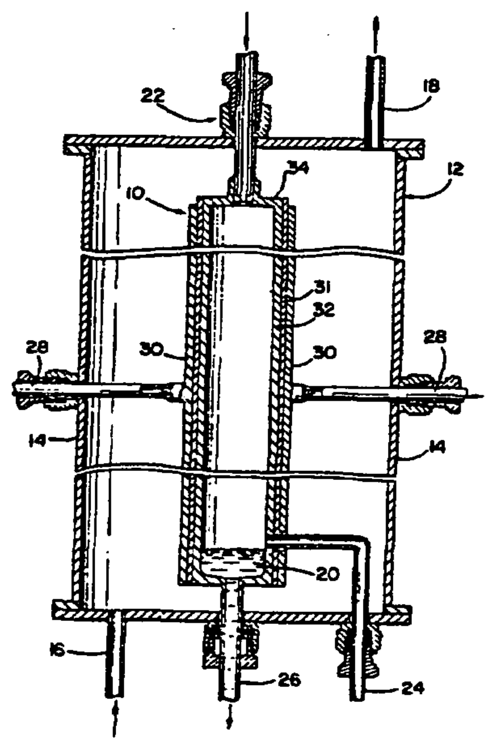
(54) Title: APPARATUS AND PROCESS FOR MAKING SOLAR GRADE SILICON

(57) Abstract

A reactor apparatus (10) adapted for continuously producing molten, solar grade purity elemental silicon by thermal reaction of a suitable precursor gas, such as silane (SiH_4). The reactor apparatus (10) includes an elongated reactor body (32) having graphite or carbon walls which are heated to a temperature exceeding themelting temperature of silicon. The precursor gas enters the reactor body (32) through an efficiently cooled inlet tube assembly (22) and a relatively thin carbon or graphite septum (44). The septum (44), being in contact on one side with the cooled inlet (22) and the heated interior of the reactor (32) on the other side, provides a sharp temperature gradient for the precursor gas entering the reactor (32) and renders the operation of the inlet tube assembly (22) substantially free of clogging. The precursor gas flows in the reactor (32) in a substantially smooth, substantially axial manner. Liquid silicon formed in the initial stages of the thermal reaction reacts with the graphite or carbon walls to provide a silicon carbide coating on the walls. The silicon carbide coated reactor is highly adapted for prolonged use for production of highly pure solar grade silicon. Liquid silicon (20) produced in the reactor apparatus (10) may be used directly in a Czochralski or other crystal shaping equipment.



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DESCRIPTION

APPARATUS AND PROCESS FOR MAKING SOLAR GRADE SILICON

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention is directed to a process and apparatus for making solar and semiconductor grade silicon by thermal reaction of a suitable precursor gas composition. More particularly, the present invention is directed to a process and apparatus for continuous production of solar and semiconductor grade silicon in the liquid phase, by thermal decomposition of a suitable precursor gas, such as silane.

2. Brief Description of the Prior Art

As is well known, highly pure elemental silicon properly doped with minute quantities of suitable doping agents, is the most widely used semiconductor and solar cell material. In view of the recent trend of increasing reliance on solar energy, there exists a significant demand for solar cell grade silicon at a reasonable cost. In fact, the present unavailability of solar cell grade silicon at a reasonable cost represents the principal factor which presently still renders solar cells too expensive for large-scale electrical power generation.

Solar cell or semiconductor grade (hereinafter solar grade) silicon is usually manufactured in a two-step chemical process. First, solid silicon compounds

abundantly available from the Earth's crust (such as SiO_2) are converted into gaseous or low boiling liquid silicon compounds such as silicon tetrachloride ($SiCl_4$), trichlorosilane ($SiHCl_3$) and silane (SiH_4). The gaseous or liquid silicon compounds are then relatively readily purified by fractional distillation or like processes.

In the next step of preparing elemental silicon of solar grade purity, the purified silicon compound is reacted in gaseous phase to yield elemental silicon, and usually a gaseous by-product. For example, silane gas is thermally decomposed in accordance with Equation I to yield silicon and hydrogen gas.

$$SiH_4 \xrightarrow[heat]{} Si + 2H_2 \qquad \text{Equation I}$$

The above-summarized processes have, hitherto, been performed in the prior art to yield solid elemental silicon. Often, the processes yield very low overall-density agglomerated particles of silicon which are hard to handle in an efficient and continuous manner. Other examples of problems associated with the gas-to-solid thermal reaction processes are: undesirable deposition of a hard silicon crust on the reactor walls, and frequent interruption of the process due to the above-noted and other problems. For example, in accordance with the most widely used prior art "Moisson" process for chemical preparation of solar grade silicon, elemental silicon is grown epitaxially on the surface of rods disposed in a reactor wherein trichlorosilane ($SiHCl_3$) and hydrogen (H_2) gases are reacted. However, even this process must be interrupted from time to time in order to remove the solid silicon deposited on the rods, and to clean the reactor.

Another significant disadvantage of the prior art chemical processes for the preparation of solid silicon is that the resulting product is usually not sufficiently large grain crystalline to be directly suitable for semiconductor or solar cell applications. Therefore, the solid silicon produced by the prior art processes must be melted in a separate step and converted in a Czochralski or like crystal pulling apparatus into large grain crystalline (ideally monocrystalline) ingots, ribbons and the like. Thus, as is well appreciated by those skilled in the art, the overall prior art processes for preparing silicon solar cells require an undesirably high input of energy.

In order to overcome or alleviate the above-noted problems, a few attempts were made in the prior art to obtain molten, rather than solid, silicon in the thermal reaction process. For example, Japanese patent application laid open for public inspection on December 2, 1977, Serial No. 52-144959, describes a process wherein a bath of molten silicon (obtained from previously-prepared solid silicon of high purity) is maintained in a reaction vessel wherein trichlorosilane ($SiHCl_3$) or silicon tetrachloride ($SiCl_4$) and hydrogen gas (H_2) are reacted. The silicon tetrachloride ($SiCl_4$) or trichlorosilane ($SiHCl_3$) is heated to 300° - 500°C, and the hydrogen gas (H_2) is heated to 1200° - 1600°C prior to introduction into the reaction vessel. The temperature is maintained in the gas containing part of the reaction vessel between 1050° to 1150°C so that solid elemental silicon is formed in the vessel by the reaction of the gases. The solid silicon, however, falls into the bath of molten silicon where it melts. A readily apparent disadvantage of the just-described

process is that it is not suitable for production of silicon from silane (SiH_4), because silane would already start significant thermal decomposition while being pre-heated prior to introduction into the reaction vessel. Furthermore, the reactants used in the process provide elemental silicon only in a relatively low yield. Still further, the process is batchwise, rather than continuous, in the sense that the gaseous reactants must be allowed to dwell in the reactor for a relatively long time to reach equilibrium. Perhaps for these and other reasons, according to the best knowledge of the present inventor, this prior art process has not gained even moderate industrial acceptance.

United States Patent Application Serial No. 126,063 filed on February 29, 1980, represents an attempt for production of molten silicon in a continuously operating reactor by thermal reaction of a suitable silicon containing precursor gas. In accordance with this disclosure, a precursor gas, such as silane, flows in an outer, forwardly moving vortex in a spiral flow reactor. A by-product gas, such as hydrogen, moves in an inner, rearwardly moving vortex. The walls of the reactor are maintained at a temperature above the melting point of silicon. Molten silicon flows downwardly on the walls of the reactor to collect in a pool wherefrom it is removed. A cooled injector tube having an internal diameter of about 0.06 inches is utilized to introduce the precursor gas tangentially relative to the interior cylindrical surface of the reactor. A vortex finder tube is disposed substantially in the center on the top of the reactor to remove the rearwardly moving vortex of the by-product gas.

The reactor described in the above-noted patent application, although designed to operate continuously for the production of molten silicon, is far from free of problems. More specifically, the injector tube is subject to frequent clogging due to formation of a solid silicon plug therein, and the emitted by-product gas contains a relatively large quantity of finely dispersed solid silicon particles.

Additional disclosures relating to the preparation of solar grade silicon are found in the following printed publications: Low-Cost Solar Array Project 5101-87, "Silicon Formation by Pyrolysis of Silane," Interim Report of the Continuous Flow Pyrolyzer Study, by H. Levin, Jet Propulsion Laboratory, California Institute of Technology, October 1978, and "Compatibility Studies of Various Refractory Materials in Contact with Molten Silicon," by O'Donnel et al., Jet Propulsion Laboratory, California Institute of Technology, March 1978 (JPL Publication 78-18).

In light of the foregoing, there still is a serious want in the prior art for a continuously operable efficient process and apparatus for chemically preparing molten silicon from a gaseous starting material. The present invention provides such a process and apparatus.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide an apparatus and process for the efficient continuous production of molten silicon from a suitable silicon containing precursor gas.

It is another object of the present invention to provide an apparatus for the continuous production of molten silicon which readily withstands prolonged exposure to molten silicon.

These and other objects and advantages are attained by a reactor apparatus wherein substantially smooth flow of a suitable silicon containing precursor gas is maintained in a substantially axial direction in an elongated reactor heated to a temperature above the melting temperature of elemental silicon. Thermal reaction of the precursor gas directly yields molten silicon which flows down on the walls of the reactor to be removed from a bottom thereof in the liquid state.

In accordance with one aspect of the present invention, an inlet tube of the reactor which injects the precursor gas into the reactor is efficiently cooled to prevent thermal formation of silicon prior to entry of the precursor gas into the reactor. One side of a relatively thin septum attached to the inlet tube is substantially in the same temperature range as the inlet tube, while the other side of the septum is exposed to the interior of the reactor and is substantially in the same temperature range as the reactor. As a result, the precursor gas entering the reactor is subjected to a very quick transition in temperature with substantially total avoidance of clogging the inlet tube by formation of a solid silicon plug.

In accordance with another aspect of the present invention, the walls of the reactor are made of graphite or carbon material which have been discovered to be quickly coated during the initial exposure of the reactor to liquid silicon with a highly resistant silicon carbide layer.

The features of the present invention can be best understood, together with further objects and advantages, by reference to the following description, taken in connection with the drawings, wherein like numerals indicate like parts.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic cross-sectional view showing the reactor apparatus of the present invention enclosed in an outer cylinder;

Figure 2 is a schematic cross-sectional view showing the reactor apparatus of the present invention;

Figure 3 is a schematic perspective view showing a precursor gas inlet tube assembly incorporated in the reactor apparatus of the present invention, and

Figure 4 is a cross-sectional view showing the precursor gas inlet tube assembly incorporated in the reactor apparatus of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The following specification taken in conjunction with the drawings sets forth the preferred embodiment of the present invention in such a manner that any person skilled in the chemical arts can use the invention. The embodiment of the invention disclosed herein is the best mode contemplated by the inventor for carrying out his invention in a commercial environment, although it should be understood that various modifications can be accomplished within the parameters of the present invention.

Referring now to the drawing Figures and particularly to the schematic cross-sectional views of Figures 1 and 2, the reactor apparatus 10 of the present invention is disclosed. The reactor apparatus 10 of the present invention is adapted for producing high purity molten silicon in a continuous process by thermal reaction of a suitable silicon containing precursor gas composition. Several known chemical reactions may be utilized in the novel process practiced in the reactor apparatus 10. For example, silicon may be produced in

the apparatus 10 by reduction of tetrachlorosilane ($SiCl_4$) or trichlorosilane ($SiHCl_3$) with hydrogen (H_2) in accordance with Equations II and III respectively.

$$SiCl_4 + 2H_2 \longrightarrow Si + 4HCl$$

Equation II

$$SiHCl_3 + H_2 \longrightarrow Si + 3HCl$$

Equation III

However, the apparatus 10 and process of the present invention is designed most advantageously for continuous production of silicon by thermal decomposition of silane gas into silicon and hydrogen gas in accordance with Equation I (set forth in the introductory section of the present application for patent). Therefore, the following exemplary description principally describes the utilization of the thermal decomposition reaction of silane in the novel apparatus and process of the present invention. Furthermore, hereinafter the term "precursor gas" is interchangeably used with the term "silane," and the term "by-product gas" is interchangeably used with the term "hydrogen." Nevertheless, it should be kept in mind that in the event the process of the present invention utilizes alternative chemical reactions (such as the reactions of Equations II or III), the precursor gas may be other than silane, and the by-product gas or gases may be other than hydrogen.

Referring now principally to Figure 1, the reactor apparatus 10 of the present invention is shown mounted in a suitable outer cylinder 12. The principal purpose of the outer cylinder 12 is to c ntain the

reactor apparatus 10 in an inert gas atmosphere while the reactor apparatus 10 is heated to high temperatures. The outer cylinder 12 may be constructed substantially in accordance with the state-of-the-art. The outer cylinder 12, of course, also provides thermal insulation for the reactor apparatus 10, and for that purpose walls 14 made of stainless steel encasing suitable insulating materials (not shown) which surround the reactor apparatus 10. Inlet and outlet tubes for the inert gas, which is preferably argon, are schematically shown on Figure 1 and bear the reference numerals 16 and 18, respectively.

The protective outer cylinder 12 also has suitable inlet ports for ducts carrying the precursor gas, the by-product gas, and the reaction product, molten silicon 20. On the schematic view of Figure 1, the inlet duct assembly for the precursor gas silane bears the reference numeral 22, the outlet duct for the by-product hydrogen the reference numeral 24, and the outlet duct for molten silicon the reference numeral 26. Finally, the outer cylinder 12 is provided with suitable entry ports for copper or like conduits 28 which conduct current for energizing graphite, "picket fence" type resistance heaters 30 surrounding the inner reactor apparatus 10. The resistance heaters 30 and the inner reactor apparatus 10 are separated from one another by a high temperature resistant electrical insulator 31.

Referring now principally to the schematic cross-sectional view of Figure 2, the inner reactor apparatus 10 is disclosed in detail. The reactor apparatus is an elongated hollow body; preferably, as is shown in the herein-described preferred embodiment, it is a hollow cylindrical body the length of which greatly exceeds its diameter. In a specific example of the reactor apparatus 10 of the present inv ntion the

cylindrical reactor body or reactor 32 is 157 cm long, and has an inner diameter of 7.6 cm. The relative length-to-width ratio of the reactor 32 is designed to provide a sufficiently long dwelling time for the gaseous reactants in the reactor 32 to reach thermodynamic equilibrium, which, under the conditions prevailing in the reactor 32, favors high yields of elemental silicon. In fact, in the apparatus of the present invention silane gas is converted in substantially one hundred percent (100%) yield to silicon.

In accordance with one important aspect of the invention, the reactor 32 is made of highly pure graphite or carbon material which rapidly reacts under the conditions prevailing in the reactor 32 with silicon to form silicon carbide (SiC). In fact, it was found in experience that the silicon formed in the initial stages of the operation of the reactor apparatus 10 is substantially consumed to react with the inner walls of the reactor 32. The resulting silicon carbide coating on the reactor walls is highly wettable by molten silicon, and is yet highly resistant to molten silicon. This is a very advantageous feature of the reactor apparatus 10 of the present invention, because it permits the formation of highly pure solar grade silicon substantially uncontaminated by material dissolved from the reactor walls.

For comparison, it is noted that liquid silicon is known in the art to be highly reactive and is often termed a "universal solvent." In fact, most prior art silicon crystal pulling apparatus struggle with the problem of keeping molten silicon sufficiently free of impurities formed when the liquid silicon reacts with or dissolves the walls of a crucible, capillary die, or the like. The present invention, however, completely solves this problem by providing the readily available graphite

or carbon reactor material, which during the process of the invention "self-converts" into the highly durable and liquid-silicon resistant silicon carbide. The initial stage of converting the carbon walls of the reactor 32 into silicon carbide is termed "priming" of the reactor.

Heating of the reactor body 32 is accomplished by the "picket fence" type resistant heaters 30 which surround the reactor body 32. In alternative embodiments of the reactor apparatus 10 of the present invention, other methods of heating may be utilized. The only critical feature of the invention regarding heating is that the interior of the reactor 32 and the interior walls are maintained above the melting temperature of silicon (1412°C) during the process of silicon production. Preferably, the interior of the reactor 32 is maintained above 1500°C, and most preferably it is maintained approximately between 1600° to 1800°C. At the operating temperatures of the reactor apparatus 10 (i.e., above 1412°C), the thermal decomposition of silane gas into silicon and hydrogen is relatively rapid. Furthermore, at this temperature the thermodynamic equilibrium favors formation of elemental silicon with substantially one hundred percent (100%) yield.

Actually, the above-noted upper limit of approximately 1800°C is not a limit of the process of the present invention, because the process may be practiced at still higher temperatures. Rather, approximately 1800°C is the upper limit of temperature that the materials of the reactor apparatus 10 of the present invention can withstand without damage.

With regard to the above-noted temperature ranges of the process of the present invention, it is further noted that conversion of the carbon or graphite walls of the reactor 32 to silicon carbide occurs below

1300°C too slowly to have any practical effect on priming the reactor 32. Therefore, in the prior art reactors operating at temperatures below 1300°C the very advantageous "priming" of the reactor does not occur to a significant extent.

Experience proved the reactor apparatus 10 of the present invention to be capable of withstanding repeated temperature cycling between ambient temperature (nonoperational time of the reactor) and 1400-1800°C (operation).

The silicon formed in the reactor 32 is in the molten phase, and flows down the silicon carbide interior walls of the reactor 32 to collect in the bottom thereof. Pure, solar grade molten silicon is drained from the bottom of the reactor 32 and is advantageously utilized, without being allowed to solidify, in a Czochralski or other crystal shaping equipment (not shown) to provide silicon ingots or ribbons (not shown).

Preferably, the reactor apparatus 10 is disposed in a substantially upright position, as is shown on Figures 1 and 2, so that flow of the molten silicon 20 on the reactor walls is gravity induced.

Referring now principally to Figures 3 and 4, the silane gas inlet duct or tube assembly 22 is disclosed in detail. The inlet tube assembly 22 is particularly adapted and highly suited for supplying silane gas into the reactor 32 in a continuous and substantially nonclogging manner. As is shown on Figure 2, the inlet tube assembly 22 is disposed substantially in the center of a top wall 34 of the reactor 32 in such a manner that the inlet tube assembly 22 is located outside of the heated interior space of the reactor 32.

The inlet tube assembly 22 comprises an elongated inlet tube 36 which is connected to a supply of silane gas. The inlet tube 36 is surrounded by a

jacket 38 wherethrough a cooling medium, such as water, is circulated. The end of the inlet tube 36 and the end of the jacket 38 together form a substantially flat substantially ring-shaped surface 40.

The ring-shaped surface 40 of the inlet tube assembly 22 is not directly exposed to the interior of the reactor 32. Rather, it is in contact with one side 42 of a carbon or graphite septum 44. The septum 44 comprises a relatively thin ring-shaped body which substantially conforms to the shape of the end of the inlet tube assembly 22. A second side 46 of the septum 44 is substantially flush with the interior surface of the top wall 34 of the reactor 32, as is shown on Figure 2.

The septum 44 insulates the inlet tube 36 from the high temperature of the reactor 32 and causes the silane gas which enters the reactor 32 to experience a very sharp temperature gradient. This is because one side 42 of the septum 44 is in contact with the efficiently cooled surface 40 of the inlet tube 36 and jacket 38, and is substantially in the same temperature range as the inlet tube 36. The other side 46 of the septum 44 is exposed to the heated interior of the reactor 32, and, being of a dark high emissivity material (porous carbon), is substantially in the same temperature range as the interior of the reactor 32.

During the process of the present invention, silane gas is continuously fed through the inlet tube assembly 22 into the reactor 32. The inlet tube assembly 22 is vigorously cooled by water circulated through the cooling jacket 38. In accordance with one important aspect of the present invention, the temperature of the silane gas introduced into the reactor 32 through the inlet tube 36 is kept at a temperature below 350°C. This is for the purpose of avoiding any significant

thermal decomposition of the silane gas, prematurely, before entry of the silane gas into the reactor 32. In order to facilitate efficient cooling of the inlet tube assembly 22, the inlet tube 36 and the jacket 38 are made of a material of high thermal conductivity, such as copper.

The relatively thin septum 44 of carbon or graphite is highly effective to avoid thermal precipitation of fine solid silicon particles on the inlet surfaces and ensuing clogging of the inlet tube and the narrow septum 44 itself. Experience has shown that during the "priming" stage of the operation of the reactor apparatus 10, the septum 44 too reacts with the newly-formed liquid silicon to form silicon carbide.

The inlet tube assembly 22 of the reactor apparatus of the present invention operates without clogging. In contrast with the prior art inlet assembly disclosed in the above-noted U.S. patent application serial number 126,063, the internal diameter of the inlet tube 36 may be quite substantial. In the herein-described specific example wherein the length of the reactor is 157 cm, the internal diameter of the inlet tube 36 is approximately 1 cm, and the diameter of the septum 44 is approximately 2.2 cm.

Dwelling time of the silane gas in the heated reactor 32 is selected in such a manner that the silane-to-liquid silicon reaction proceeds to substantially reach thermodynamic equilibrium which favors complete decomposition. During the process, the silane gas and the by-product hydrogen gas flow in a substantially smooth, substantially unperturbed flow substantially axially in the reactor 32. The lower, reservoir portion of the reactor 32, containing molten silicon 20, is kept at a temperature exceeding the melting temperature of silic n. The molten silic n may be continuously drained

out of the reactor apparatus 10 through the outlet duct assembly 26 which may be constructed in accordance with state of the art. The by-product hydrogen gas leaves the reactor 32 through the hydrogen outlet duct assembly 24 which is located on a side wall 14 of the reactor 32 above the level of molten silicon 20.

Principal advantages of the above-described reactor apparatus and process of the present invention include the following. The reactor 32 is readily manufactured of relatively inexpensive pure carbon or graphite material, and yet readily "primes" or converts itself to eventually expose only non-contaminating silicon carbide for contact with the highly pure, solar grade silicon. The reactor is capable of continuous, trouble-free operation, is not subject to clogging due to buildup of solid silicon material, and does not require continuous scraping or clearing operation to keep the walls free of deposited hard crust of silicon.

The above-described specific embodiment of the reactor apparatus 10 is capable of producing several kilograms (up to 15 Kg) of solar grade molten silicon per hour. For a still larger scale silicon producing plant a still larger embodiment of the reactor apparatus 10 of the present invention may be utilized. Alternatively, and preferably several reactors of approximately of the above-noted specific dimensions may be operated simultaneously.

Furthermore, the molten silicon chemically obtained in the process of the present invention may be directly fed into a Czochralski or other crystal shaping apparatus (not shown), eliminating the need for remelting of solid silicon.

Several modifications of the above-described apparatus and process may become readily apparent to those skilled in the art in light of the above disclosure. Therefore, the scope of the present invention should be interpreted solely from the following claims.

WHAT IS CLAIMED IS:

1. A reactor apparatus for making elemental silicon by thermal reaction of a precursor gas such as silane, to yield silicon and a by-product gas, such as hydrogen, the apparatus comprising:

a reactor having walls defining a reactor space;

heating means for heating the walls of the reactor so as to provide an internal temperature in the reactor space which exceeds the melting temperature of silicon;

precursor gas inlet means operatively associated with the reactor for introducing the precursor gas into the reactor space and for keeping the temperature of the precursor gas below thermal decomposition temperature of the precursor gas until said precursor gas effectively enters the heated reactor space;

by-product gas outlet means for outletting the by-product gas from the reactor space, and

molten silicon outlet means operatively associated with the reactor for outletting the produced molten silicon from the reactor, the precursor gas inl t means and the by-product gas outl t m ans

being disposed relative to one another so as to provide a substantially smooth flow of the precursor gas in the reactor.

2. The reactor apparatus of Claim 1 wherein the heating means are adapted for maintaining the internal temperature approximately between 1500-1800°C.

3. The reactor apparatus of Claim 2 wherein the heating means are adapted for maintaining the internal temperature approximately between 1600-1800°C.

4. The reactor apparatus of Claim 1 wherein the walls of the reactor comprise carbon or graphite material capable of reacting with molten silicon to form silicon carbide and to provide at least a coating of silicon carbide on said walls.

5. The reactor apparatus of Claim 1 wherein the reactor comprises a cylinder.

6. The reactor apparatus of Claim 1 wherein the reactor comprises a substantially upright-standing elongated hollow body, and wherein the inlet means are adapted for introducing the precursor gas substantially on top of the elongated body to provide a substantially axial flow of gas therein.

7. The reactor apparatus of Claim 6 wherein the molten silicon outlet means are adapted for permitting gravity-induced outflow of molten silicon substantially from the bottom of the elongated body.

8. The reactor apparatus of Claim 7 wherein the reactor comprises an elongated cylindrical hollow body.

9. The reactor apparatus of Claim 1 wherein the inlet means comprise an efficiently cooled inlet tube wherethrough the precursor gas flows, and septum means in contact on one side thereof with the cooled inlet tube and exposed on another side thereof to the heated reactor space, the septum means being adapted for being at a temperature above the melting point of silicon on the exposed side thereof.

10. The reactor apparatus of Claim 9 wherein the septum means comprise an annular body of carbon or graphite.

11. The reactor apparatus of Claim 9 wherein the inlet means comprise a copper tube provided with jacket means for circulating a cooling medium in the jacket means.

12. A reactor apparatus for thermal decomposition of silane gas directly into molten silicon, the apparatus comprising:

an elongated reactor having walls made of carbon or graphite material, and enclosing a reactor space;

heating means operatively associated with the reactor for maintaining the temperature in the reactor space above the melting temperature of silicon;

silane gas inlet means for introducing a gas composition containing at least a significant perc ntag of silane gas

into the reactor for a substantially smooth substantially axial flow in said reactor, the inlet means also comprising cooling means for maintaining the gas composition at a temperature below the decomposition temperature of silane gas until the gas composition is effectively disposed in the heated reactor space;

gas outlet means operatively associated with the reactor and disposed remotely from said inlet means for outletting any unreacted gas and by-product gas from said reactor space while said substantially axial gas flow is maintained, and

molten silicon outlet means operatively associated with reactor for outletting the molten silicon product from the reactor.

13. The reactor apparatus of Claim 12 wherein the heating means are adapted for maintaining the temperature in the reactor space approximately between 1500-1800°C.

14. The reactor apparatus of Claim 13 wherein the heating means are adapted for maintaining the temperature in the reactor space approximately between 1600-1800°C.

15. The reactor apparatus of Claim 12 wherein the reactor comprises a substantially cylindrical hollow body.

16. The reactor apparatus of Claim 12 wherein the reactor is a substantially upright-standing elongated body, wherein the inlet means are disposed substantially in a top portion of said body, and wherein the molten silicon outlet means are disposed substantially in the bottom of said body.

17. The reactor apparatus of Claim 12 wherein the inlet means comprise a tube disposed substantially outside of the heated reactor space, said tube being cooled by the cooling means, the inlet means further comprising insulating septum means in contact with the tube and also exposed to the heated space of the reactor, the exposed portion of the septum means being substantially above the melting temperature of silicon.

18. The reactor apparatus of Claim 17 wherein the septum means comprise an annular body of carbon or graphite having one side in contact with a discharge end of the tube and another side exposed to the reactor space.

19. A process for directly producing molten silicon by thermal reaction of a suitable precursor gas composition in a reaction chamber, the process comprising the steps of:

maintaining an interior of the reaction chamber in a first temperature range which is substantially above the melting point of silicon;

maintaining a substantially smooth flow of the precursor gas composition in the reaction chamber while permitting the precursor gas composition to undergo thermal r action to yi ld molten silicon;

allowing unreacted gas precursor composition and by-product gas to exit from the reaction chamber, and

allowing molten silicon to exit from the reaction chamber.

20. The process of Claim 19 wherein the first temperature range is approximately between 1500-1800°C.

21. The process of Claim 20 wherein the first temperature range is approximately between 1600-1800°C.

22. The process of Claim 19 wherein the second temperature range is below 350°C.

23. The process of Claim 19 wherein the precursor gas composition comprises silane.

24. The process of Claim 19 further comprising a step of maintaining the gas composition in a second temperature range which is below the thermal reaction temperature of the precursor gas composition, and further comprising a step of passing the precursor gas composition through a cooled inlet tube wherein said second temperature range is maintained prior to introducing the precursor gas composition into the heated reaction chamber.

25. The process of Claim 24 wherein the step of introducing comprises a step of passing the gas composition through a relatively thin septum having at one end thereof, adjacent to the cooled inlet tube, a temperature substantially in the second temperature range, and at another end thereof, adjacent to the

interior of the reaction chamber, a temperature substantially in the first temperature range.

26 The process of Claim 25 wherein the precursor gas composition comprises silane.

27 The process of Claim 24 wherein the septum comprises carbon or graphite material.

28. The process of Claim 19 wherein the substantially smooth flow is a substantially axial downward flow substantially parallel with the Earth's gravitational force field.

29. A process for directly producing molten silicon by thermal decomposition of silane gas in a reactor having carbon or graphite walls, the process comprising the steps of:

maintaining the interior temperature of the reactor approximately between 1500-1800°C;

maintaining a gas composition including at least a significant amount of silane gas below approximately 350°C.

abruptly raising the temperature of the gas composition from below 350°C to above approximately 1500°C by suddenly introducing the gas composition into the interior of the reactor;

maintaining a substantially smooth substantially axial flow of the gas composition in the reactor whereby the silane gas thermally decomposes into molten silicon and hydrogen gas and whereby

carbon or graphite walls of the reactor gradually react with the molten silicon to form silicon carbide;

allowing the unreacted gas composition and by-product hydrogen gas to exit from the reactor, and

allowing the produced molten silicon to exit from the reactor in a liquid state.

30. The process of Claim 23 wherein the axial flow of the gas composition is a downward flow substantially parallel with the Earth's gravitational force vector.

31. The process of Claim 30 wherein the step of maintaining the gas composition below 350°C includes a step of passing the gas composition through a cooled inlet tube leading to the reactor but located outside of the heated interior of the reactor.

32. The process of Claim 31 wherein the step of abruptly raising the temperature includes a step of passing the gas composition through a relatively thin septum into the interior of the reactor, one end of said septum being in contact with the cooled inlet tube and substantially in the same temperature range as the inlet tube, another end of the septum being adjacent to the interior of the reactor and substantially in the same temperature range as the interior.

33. The process of Claim 32 wherein the septum comprises carbon or graphite, whereby molten silicon reacts with the septum to form silicon carbide.

AMENDED CLAIMS

[received by the International Bureau on 07 November 1983 (07.11.83); original claims 1 to 33 replaced by amended claims 1 to 35]

1. A reactor apparatus for making elemental silicon by thermal reaction of a silicon containing precursor gas such as silane, to yield silicon and a by-product gas, such as hydrogen, the apparatus comprising:

a reactor having walls defining a reactor space;

heating means for heating the walls of the reactor so as to provide an internal temperature in the reactor space which exceeds the melting temperature of silicon;

cooled precursor gas inlet means located outside said reaction chamber and operatively associated with the reactor for introducing the precursor gas into the reactor space and for keeping the temperature of the precursor gas below thermal decomposition temperature of the precursor gas until said precursor gas enters the heated reactor space;

by-product gas outlet means for outletting the by-product gas from the reactor space, and

molten silicon outlet means operatively associated with the reactor for outletting the produced molten silicon from the reactor, the precursor gas inlet means and the by-product gas outlet means being disposed relative to one another so as to provide a substantially smooth flow of the precursor gas in the reactor.

2. The reactor apparatus of Claim 1 wherein the heating means are adapted for maintaining the internal temperature approximately between 1500-1800°C.

3. The reactor apparatus of Claim 2 wherein the heating means are adapted for maintaining the internal temperature approximately between 1600-1800°C.

4. The reactor apparatus of Claim 1 wherein the walls of the reactor comprise carbon or graphite material capable of rapidly reacting with molten silicon to convert to silicon carbide.

5. The reactor apparatus of Claim 1 wherein the reactor comprises a cylinder.

6. The reactor apparatus of Claim 1 wherein the reactor comprises a substantially upright-standing elongated hollow body, and wherein the inlet means are adapted for introducing the precursor gas substantially on top of the elongated body to provide a substantially axial flow of gas therein.

7. The reactor apparatus of Claim 6 wherein the molten silicon outlet means are adapted for permitting gravity-induced outflow of molten silicon substantially from the bottom of the elongated body.

8. The reactor apparatus of Claim 7 wherein the reactor comprises an elongated cylindrical hollow body.

9. The reactor apparatus of Claim 1 wherein the inlet means comprise an efficiently cooled inlet tube wherethrough the precursor gas flows, and septum means in contact on one face thereof with the cooled inlet tube and exposed on the opposite face thereof to the heated reactor space, the septum means being adapted for being at a temperature above the melting point of silicon on the exposed face thereof.

10. The reactor apparatus of Claim 9 wherein the septum means comprise an annular body of carbon or graphite.

11. The reactor apparatus of Claim 9 wherein the inlet means comprise a copper tube provided with jacket means for circulating a cooling medium in the jacket means.

12. A reactor apparatus for thermal decomposition of silane gas directly into molten silicon, the apparatus comprising:

an elongated reactor having walls made of carbon or graphite material, and enclosing a reactor space;

heating means operatively associated with the reactor for maintaining the temperature in the reactor space above the melting temperature of silicon;

silane gas inlet means for introducing a gas composition containing at least a significant percentage of silane gas into the reactor for a substantially smooth substantially axial flow in said reactor, the inlet means being located outside the reaction chamber and also comprising cooling means for maintaining the gas composition at a temperature below the decomposition temperature of silane gas until the gas composition is in the heated reactor space;

gas outlet means operatively associated with the reactor and disposed remotely from said inlet means for outletting any unreacted gas and by-product gas from said reactor space while said substantially axial gas flow is maintained, and

molten silicon outlet means operatively associated with reactor for outletting the molten silicon product from the reactor.

13. The reactor apparatus of Claim 12 wherein the heating means are adapted for maintaining the temperature in the reactor space approximately between 1500-1800°C.

14. The reactor apparatus of Claim 13 wherein the heating means are adapted for maintaining the temperature in the reactor space approximately between 1600-1800°C.

15. The reactor apparatus of Claim 12 wherein the reactor comprises a substantially cylindrical hollow body.

16. The reactor apparatus of Claim 12 wherein the reactor is a substantially upright-standing elongated body, wherein the inlet means are disposed substantially in a top portion of said body, and wherein the molten silicon outlet means are disposed substantially in the bottom of said body.

17. The reactor apparatus of Claim 12 wherein the inlet means comprise a tube disposed substantially outside of the heated reactor space, said tube being cooled by the cooling means, the inlet means further comprising insulating septum means in contact with the tube and also exposed to the heated space of the reactor, the exposed portion of the septum means being substantially above the melting temperature of silicon.

18. The reactor apparatus of Claim 17 wherein the septum means comprise an annular body of carbon or graphite having one face in contact with a discharge end of the tube and the opposite face exposed to the reactor space.

19. A process for directly producing molten silicon by thermal reaction of a silicon containing precursor gas composition in a reaction chamber, the process comprising the steps of:

maintaining said gas composition in a first temperature range below the thermal reaction temperature of said gas composition;

maintaining the reaction chamber in a second temperature range above the melting point of silicon;

abruptly raising the temperature of said gas composition from said first temperature range to said second temperature range by introducing said gas composition through a cooled inlet means located outside said reaction chamber;

maintaining a substantially smooth axial flow of the precursor gas composition in the reaction chamber while permitting the precursor gas composition to undergo thermal reaction to yield molten silicon;

allowing unreacted precursor gas composition and by-product gas to exit from the reaction chamber, and

allowing molten silicon to exit from the reaction chamber.

20. The process of Claim 19 wherein the second temperature range is approximately 1500-1800°C.

21. The process of Claim 20 wherein the second temperature range is approximately 1600-1800°C.

22. The process of Claim 19 wherein the first temperature range is below 350°C.

23. The process of Claim 19 wherein the precursor gas composition comprises silane.

24. The process of Claim 19 wherein said cooled inlet means is a tube.

25. The process of Claim 19 wherein abruptly raising the temperature of said precursor gas further comprises passing said gas composition from said cooled inlet means through a thin septum having one face adjacent said cooled inlet means and in said first temperature range, and the opposite face flush with the wall forming said reaction chamber and in said second temperature range.

26. The process of Claim 25 wherein said septum is made of a high emissivity material.

27. The process of Claim 25 wherein the precursor gas composition comprises silane.

28. The process of Claim 25 wherein the septum comprises carbon or graphite material whereby molten silicon reacts with the septum to convert to silicon carbide on the opposite face thereof.

29. The process of Claim 19 wherein the substantially smooth flow is a substantially axial downward flow substantially parallel with the Earth's gravitational force field.

30. A process for directly producing molten silicon by thermal decomposition of silane gas in a reactor made of carbon or graphite walls, the process comprising the steps of:

maintaining the interior temperature of the reactor approximately between 1500-1800°C.

maintaining a gas composition including at least a significant amount of silane gas below approximately 350°C.;

abruptly raising the temperature of the gas composition from below 350°C. to above approximately 1500°C. by suddenly introducing the gas composition into the interior of the reactor from a cooled inlet means outside the interior of the reactor;

maintaining a substantially smooth substantially axial flow of the gas composition in the reactor whereby the silane gas thermally decomposes into hydrogen gas and solid silicon particles that quickly become molten whereby the inner carbon or graphite walls of the reactor rapidly react with the molten silicon to convert to silicon carbide;

allowing the unreacted gas composition and by-product hydrogen gas to exit from the reactor; and

allowing the produced molten silicon to exit from the reactor in a liquid state.

31. The process of Claim 30 wherein the axial flow of the gas composition is a downward flow substantially parallel with the Earth's gravitational force vector.

32. The process of Claim 30 wherein said cooled inlet means comprises a cooled inlet tube.

33. The process of Claim 32 wherein the step of abruptly raising the temperature includes a step of passing the gas composition through a relatively thin septum into the interior

of the reactor, one face of said septum being in contact with the cooled inlet tube and substantially in the same temperature range as the inlet tube, the other face of the septum being flush with the interior wall of the reactor and substantially in the same temperature range as the interior.

34. The process of Claim 33 wherein said septum is made of a high emissivity material.

35. The process of Claim 33 wherein the septum comprises carbon or graphite, whereby molten silicon reacts with the septum to convert to silicon carbide.

FIG. 1

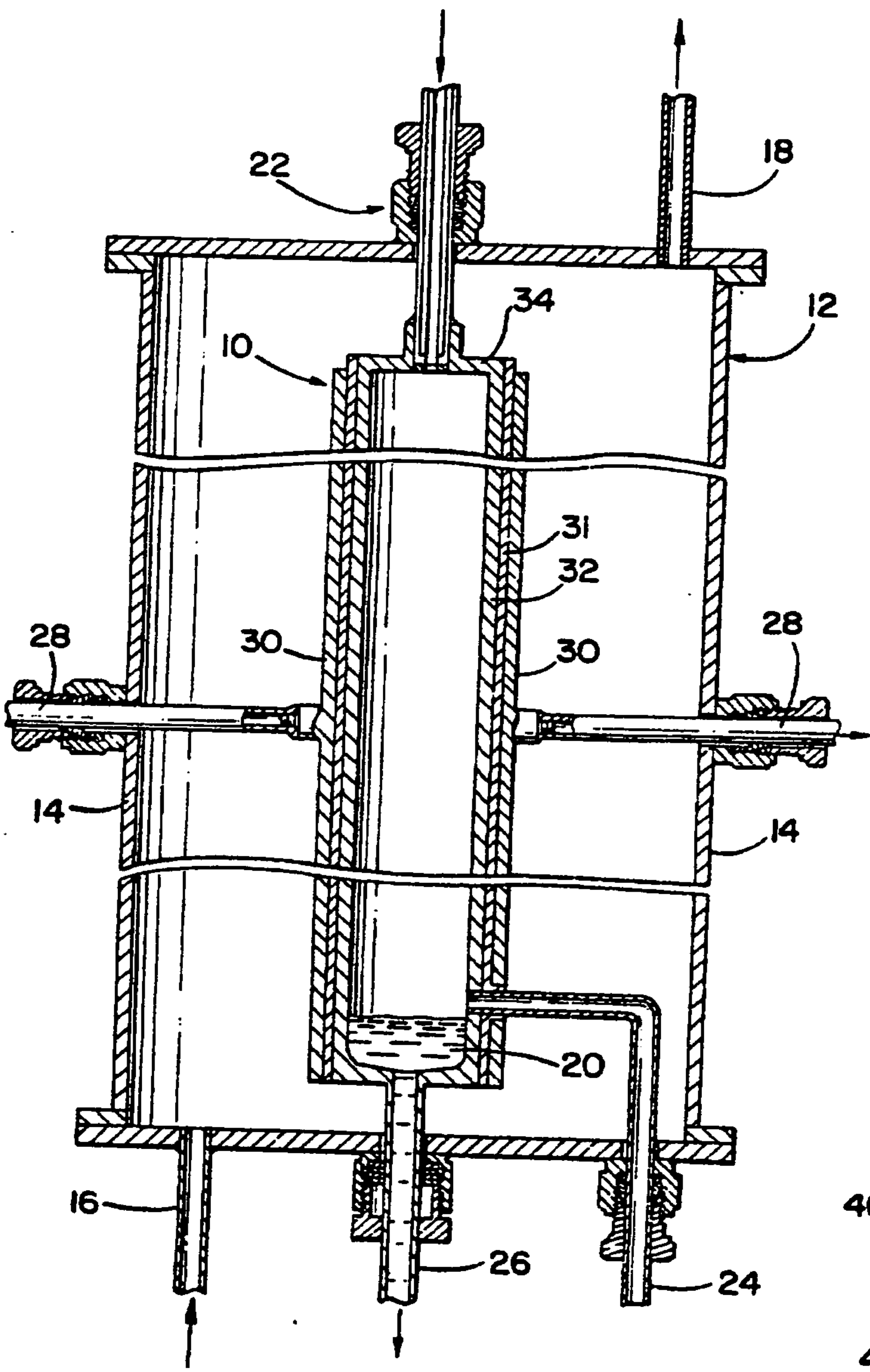


FIG. 3

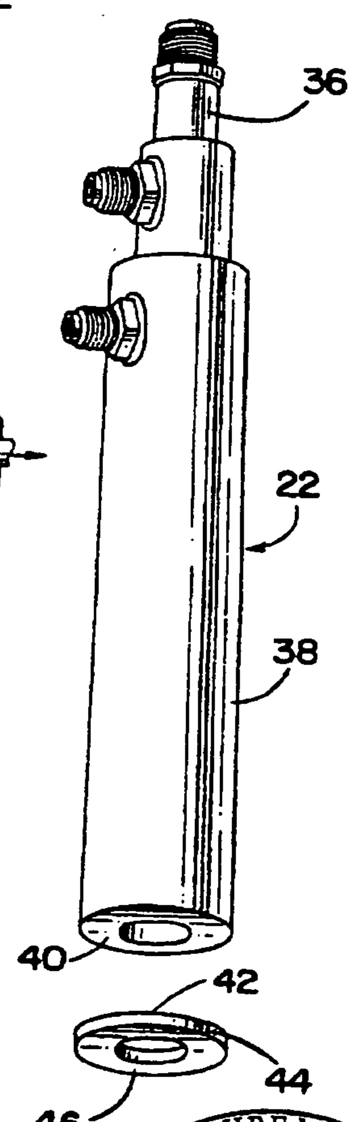


FIG. 2

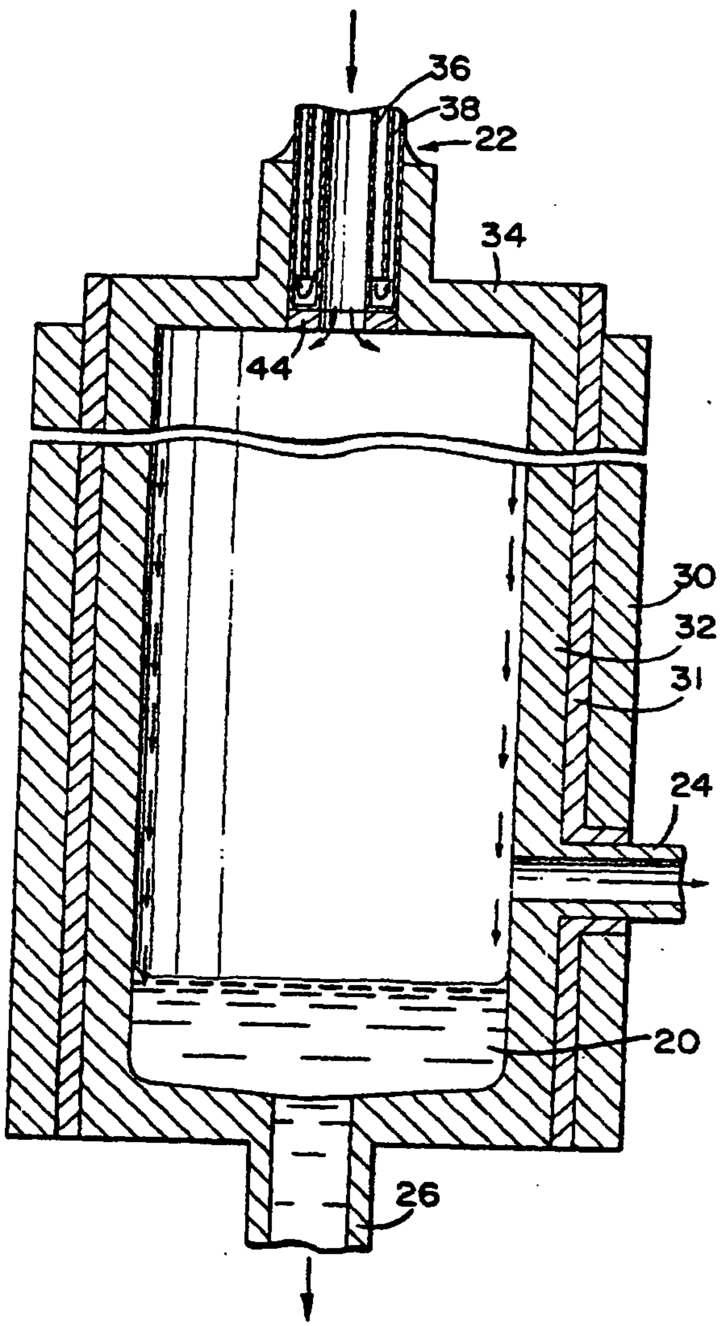
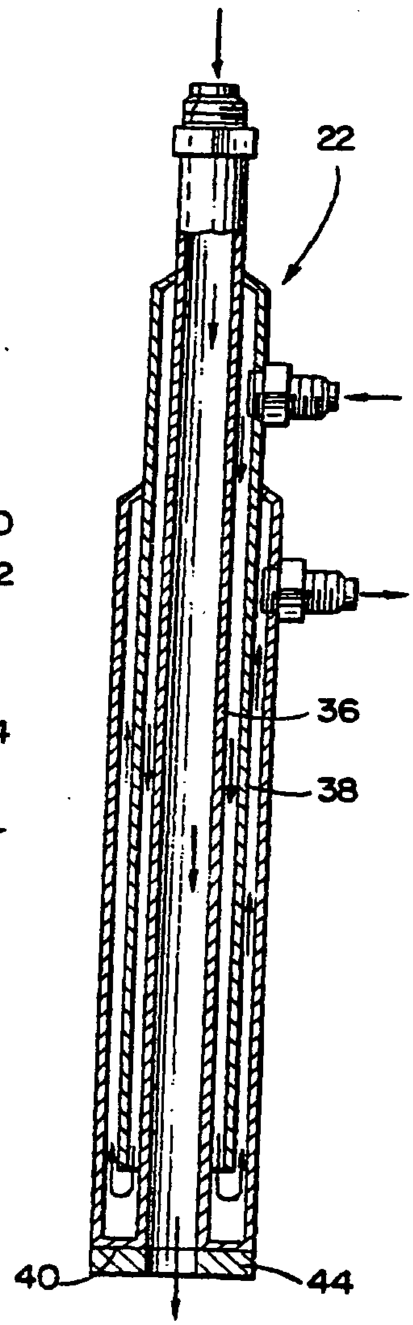


FIG. 4



INTERNATIONAL SEARCH REPORT

International Application No PCT/US83/00944

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)

According to International Patent Classification (IPC) or to both National Classification and IPC

INT. CL.3 C01B 33/02; C09C 3/00

U.S. CL. 423/349; 422/158

II. FIELDS SEARCHED

Minimum Documentation Searched

Classification System	Classification Symbols
US	423/349, 350 118/716 156/Dig. 64 422/129, 158, 209, 241

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched

III. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
Y,P	US, A, 4,343,772, (Levin et al) 10 August 1982	1-32
A,P	US, A, 4,342,284, (Loser et al), 3 August 1982	1-32
A	N, DOE/JPL 954471 79/12, issued 10 December 1979, Nanis et al.	4,10, 28-31
A	N, ERDA/JPL 954471-77/3, issued November 1978, Kapur et al.	4,10, 28-31

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
30 August 1983	07 SEP 1983
International Searching Authority	**Signature of Authorized Officer**
ISA/US	Steven Capella Steven Capella

Form PCT/ISA/210 (second sheet) (October 1981)

International Application No. PCT/US83/00944

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [10]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers ...., because they relate to subject matter [12] not required to be searched by this Authority, namely:

2. ☐ Claim numbers ...., because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out [13], specifically:

VI. ☒ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [11]

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☒ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.